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# Identification and emission factors of molecular tracers in organic aerosols from biomass burning Part 2. Deciduous trees

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## Abstract

Smoke particulate matter from deciduous trees (angiosperms) subjected to controlled burning, both under smoldering and flaming conditions, was sampled by high volume air filtration on precleaned quartz fiber filters. The filtered particles were extracted with dichloromethane and the crude extracts were methylated for separation by thin layer chromatography into hydrocarbon, carbonyl, carboxylic acid ester and polar fractions. Then, the total extract and individual fractions were analyzed by gas chromatography and gas chromatography–mass spectrometry. The major organic components directly emitted in smoke particles were straight chain aliphatic compounds from vegetation wax and triterpenoid acids (biomarkers) from gums and mucilages. The major natural products altered by combustion included derivatives from phenolic (lignin) and monosaccharide (cellulose) biopolymers and oxygenated and aromatic products from triterpenoids. Steroid biomarkers and polycyclic aromatic hydrocarbons (PAH) were also present, however, as minor constituents. Although the concentrations of organic compounds in smoke aerosols are highly variable and dependent on combustion temperature, the biomarkers and their combustion alteration products are in these cases source specific. The major components are adsorbed or trapped on particulate matter and thus may be utilized as molecular tracers in the atmosphere for determining fuel type and source contributions from biomass burning. © 2001 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Emission factors have only been determined for a limited number of biomass smoke samples (i.e. mainly conifers; Rogge et al., 1998; Schauer et al., 2000; Simoneit et al., 2000; Oros and Simoneit, 2001). Thus, more information on deciduous trees is necessary for modeling biomass burn emissions in air basins or air masses. The aim of this study is to report the organic chemical

composition of smoke particulate matter emitted by flaming and smoldering combustion of fuel from deciduous trees (angiosperms). This study is Part 2 of the companion report on the chemical composition of smoke from burning of temperate climate conifers (Oros and Simoneit, 2001). In general, each individual plant species emits a “chemical fingerprint” of natural and thermally altered organic constituents upon burning, which is source specific and unique in composition. The incomplete thermal combustion of organic natural product precursors results in emission products which still retain structural characteristics of the precursors (molecular markers). From these products it is possible to determine precursor/product relationships and reaction pathways. The dominant directly emitted and thermally altered molecular markers may be used as specific

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tracers for tracking emissions specifically from angiosperm burning.

## 2. Experimental methods

Samples were collected from temperate and polar region forested zones, away from urban areas and major roads (Table 1). The branches (1–2 cm diameter), leaves (dry and green), with gums and mucilages were collected from various levels in the canopy of each single tree species. All vegetation samples were placed in paper bags and allowed to dry over a 2 week period. Weight measurements were taken before and after burning in order to determine the total mass of plant material consumed. The details of the experimental methods, which include smoke collection, sample extraction, fractionation, instrumental analyses, compound identification and quantitation, are described in Part 1 (Oros and Simoneit, 2001).

## 3. Results and discussion

The major organic components identified in the soluble lipid fraction of the deciduous tree smoke samples and their emission factors ( $\mu\text{g}/\text{kg}$  of deciduous tree fuel burned) are given in Table 2. The emission factors are preliminary because only one burning test was conducted for each deciduous tree species included in this study. The distributions of the molecular classes include the following: homologous series of aliphatic compounds (*n*-alkanoic acids, *n*-alkanones, *n*-alkanols, *n*-alkanes and *n*-alkenes); polycyclic aromatic hydrocarbons (PAH); monosaccharides from cellulose; methoxyphenols from lignin; and steroid and terpenoid (mainly triterpenoid) biomarkers. The distributions and abundances of the angiosperm smoke constituents are strongly dependent on combustion conditions (e.g. smoldering versus flaming, duration). Thus, the values reported here should not be used as absolute but as relative chemical fingerprints for these sources. The biomarkers are source specific and may be used as confirming tracers for transport and fate studies of deciduous tree smoke emissions in the environment.

### 3.1. Homologous compound series

Examples of the typical GC–MS TIC (total ion current) traces for the total extract and TLC fractions of deciduous tree smoke samples (Eucalyptus, Oregon Maple, Red Alder, Silver Birch and Dwarf Birch, Table 1) are given in Figs. 1–5. The TIC traces of the total extracts of the smoke samples show the distributions and relative abundances of the major organic constituents, while the TIC traces of the TLC fractions F1–F4 show the distributions and abundances of the aliphatics, aromatics and molecular biomarkers separated according to functional group and polarity properties. The TLC separation procedure was conducted on all smoke samples in order to best identify a source specific chemical fingerprint that is representative of deciduous tree smoke emissions. Thus, the discussion will focus on the identity and distributions (C number range and maxima,  $C_{\text{max}}$ , and C preference indices, CPI; Mazurek and Simoneit, 1984) of the major aliphatic homologs and biomarkers.

#### 3.1.1. *n*-Alkanes

The distribution of *n*-alkanes in deciduous tree smoke (Table 2, also see examples in Figs. 1b–5b) ranges in C chain length from  $C_{14}$  to  $C_{35}$  and shows an odd to even C number predominance (CPI range from 2.6 to 6.8, average = 5.3). The  $C_{\text{max}}$  for the *n*-alkanes range from 25 to 29 and confirm a significant input from epicuticular wax sources. Vascular plants synthesize epicuticular waxes containing odd C number *n*-alkanes usually in the  $C_{25}$ – $C_{33}$  range with  $C_{29}$  or  $C_{31}$  as dominant homologs which often contribute up to 90% of all paraffins found in plant waxes (Kolattukudy, 1970).

#### 3.1.2. *n*-Alkenes

The *n*-alkenes are primarily terminal olefins (i.e. alk-1-enes). They range from  $C_{14}$  to  $C_{29}$ , with an even to odd C number predominance (CPI range from 0.2 to 0.9, average = 0.3), and various  $C_{\text{max}}$  at 22, 25 and 26 (Table 2, also Fig. 1b). Alkenes are not major components in plant waxes and their origin has been inferred to be from biomass fuel (Abas et al., 1995). The *n*-alkenes are formed primarily by the thermal dehydration of *n*-alkanols (which have an even C number predominance,

Table 1  
Deciduous tree species sampled for biomass burning in this study

Common name	Botanical name	Collection region
Dwarf Birch	<i>Betula glandulosa</i>	Shingle Point, Yukon Territory
Eucalyptus	<i>Eucalyptus dalrympleana</i>	Arcata, CA
Oregon Maple	<i>Acer macrophyllum</i>	Gold Beach, OR
Red Alder	<i>Alnus rubra</i>	Mary's Peak, Philomath, OR
Silver Birch	<i>Betula pendula</i>	Willamette Valley, Corvallis, OR

Table 2

Emission factors (mg/kg of deciduous tree fuel burned) of the major organic constituents in smoke<sup>a</sup>

Compound name	Composition	M.W.	Eucalyptus	Oregon Maple	Red Alder	Silver Birch	Dwarf Birch	ID Basis <sup>b</sup>
<i>I. Homologous series</i>								
<i>n-Alkanes</i>								
<i>(Natural products)</i>								
<i>n</i> -Tetradecane	C <sub>14</sub> H <sub>30</sub>	198		79		782		A
<i>n</i> -Pentadecane	C <sub>15</sub> H <sub>32</sub>	212		195		1568		A
<i>n</i> -Hexadecane	C <sub>16</sub> H <sub>34</sub>	226		121		1428		A
<i>n</i> -Heptadecane	C <sub>17</sub> H <sub>36</sub>	240		253		2201		A
<i>n</i> -Octadecane	C <sub>18</sub> H <sub>38</sub>	254	169	396	138	1909	65	A
<i>n</i> -Nonadecane	C <sub>19</sub> H <sub>40</sub>	268	291	537	342	2562	331	A
<i>n</i> -Eicosane	C <sub>20</sub> H <sub>42</sub>	282	383	833	526	3164	614	A
<i>n</i> -Heneicosane	C <sub>21</sub> H <sub>44</sub>	296	722	1031	926	3706	1235	A
<i>n</i> -Docosane	C <sub>22</sub> H <sub>46</sub>	310	898	1249	1792	184	2362	A
<i>n</i> -Tricosane	C <sub>23</sub> H <sub>48</sub>	324	1437	1174	2024	996	2591	A
<i>n</i> -Tetracosane	C <sub>24</sub> H <sub>50</sub>	338	1186	1313	1412	14377	3569	A
<i>n</i> -Pentacosane	C <sub>25</sub> H <sub>52</sub>	352	3088	2313	11753	66272	8025	A
<i>n</i> -Hexacosane	C <sub>26</sub> H <sub>54</sub>	366	632	505	1149	721	4420	A
<i>n</i> -Heptacosane	C <sub>27</sub> H <sub>56</sub>	380	3056	13179	19293	64090	25977	A
<i>n</i> -Octacosane	C <sub>28</sub> H <sub>58</sub>	394	496	3075	692	1084	2268	A
<i>n</i> -Nonacosane	C <sub>29</sub> H <sub>60</sub>	408	3064	21521	3523	15076	15879	A
<i>n</i> -Triacontane	C <sub>30</sub> H <sub>62</sub>	422	1149	1289	139	2429	1262	A
<i>n</i> -Hentriacontane	C <sub>31</sub> H <sub>64</sub>	436	1725	8381	1678	20986	23860	A
<i>n</i> -Dotriacontane	C <sub>32</sub> H <sub>66</sub>	450	163	738		1005	710	A
<i>n</i> -Tritriacontane	C <sub>33</sub> H <sub>68</sub>	464	495	1548		1166	1931	A
<i>n</i> -Tetratriacontane	C <sub>34</sub> H <sub>70</sub>	478	266					A
<i>n</i> -Pentatriacontane	C <sub>35</sub> H <sub>72</sub>	492	193					A
Total <i>n</i> -alkanes			19414	59731	45388	205704	95098	
CPI			2.6	5.2	6.8	6.6	5.2	
Cmax			25	29	27	25	27	
<i>n-Alkenes</i>								
<i>(Alteration products)</i>								
<i>n</i> -Tetradec-1-ene	C <sub>14</sub> H <sub>28</sub>	196				556	414	A
<i>n</i> -Pentadec-1-ene	C <sub>15</sub> H <sub>30</sub>	210				1722		A
<i>n</i> -Hexadec-1-ene	C <sub>16</sub> H <sub>32</sub>	224	233	78		3234		A
<i>n</i> -Heptadec-1-ene	C <sub>17</sub> H <sub>34</sub>	238	98	69		2786		A
<i>n</i> -Octadec-1-ene	C <sub>18</sub> H <sub>36</sub>	252	206	259		3550	3604	A
<i>n</i> -Nonadec-1-ene	C <sub>19</sub> H <sub>38</sub>	266	311	380		5261	303	S
<i>n</i> -Eicos-1-ene	C <sub>20</sub> H <sub>40</sub>	280	361	794	250	3907	622	A
<i>n</i> -Heneicos-1-ene	C <sub>21</sub> H <sub>42</sub>	294	437	476	265	6472	866	S
<i>n</i> -Docos-1-ene	C <sub>22</sub> H <sub>44</sub>	308	1762	468	1164	19081	3291	S
<i>n</i> -Tricos-1-ene	C <sub>23</sub> H <sub>46</sub>	322	426	536	289	625	1232	S
<i>n</i> -Tetracos-1-ene	C <sub>24</sub> H <sub>48</sub>	336	1665	698	770	537	4092	S
<i>n</i> -Pentacos-1-ene	C <sub>25</sub> H <sub>50</sub>	350	130	131		19879	2079	S
<i>n</i> -Hexacos-1-ene	C <sub>26</sub> H <sub>52</sub>	364	1639	4291	363	11434	7120	S
<i>n</i> -Heptacos-1-ene	C <sub>27</sub> H <sub>54</sub>	378				2481		S
<i>n</i> -Octacos-1-ene	C <sub>28</sub> H <sub>56</sub>	392	496			3939		A
<i>n</i> -Nonacos-1-ene	C <sub>29</sub> H <sub>58</sub>	406				634		S
Total <i>n</i> -alkenes			7763	8180	3100	86099	23622	
CPI			0.2	0.2	0.2	0.9	0.2	
Cmax			22	26	22	25	26	
<i>Carboxylic acids</i>								
<i>(Natural products)</i>								
<i>n</i> -Octanoic acid	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	144	953	4255		7264		S
<i>n</i> -Nonanoic acid	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	158	1250	4853	1699	4367		S

(continued on next page)

Table 2 (continued)

Compound name	Composition	M.W.	Eucalyptus	Oregon Maple	Red Alder	Silver Birch	Dwarf Birch	ID Basis <sup>b</sup>
<i>n</i> -Decanoic acid	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	172	295	3015		2225		S
<i>n</i> -Undecanoic acid	C <sub>11</sub> H <sub>22</sub> O <sub>2</sub>	186	508	999		1610		S
<i>n</i> -Dodecanoic acid	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	200	553	7104	1634	3662	1283	S
<i>n</i> -Tridecanoic acid	C <sub>13</sub> H <sub>26</sub> O <sub>2</sub>	214	361	1107	725	2584	1193	S
<i>n</i> -Tetradecanoic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	228	2967	30258	6475	18815	20667	S
<i>n</i> -Pentadecanoic acid	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	242	1532	4073	4102	7064	5742	S
<i>n</i> -Hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	256	18058	97969	62887	90225	172686	A
<i>n</i> -Heptadecanoic acid	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	270	1297	6733	3914	7127	7821	S
<i>n</i> -Octadecanoic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	284	4340	21460	8326	14242	48503	S
<i>n</i> -Nonadecanoic acid	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	298	513	3898	2664	3414	5452	S
<i>n</i> -Eicosanoic acid	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	312	5248	3898	7352	9894	55822	S
<i>n</i> -Heneicosanoic acid	C <sub>21</sub> H <sub>42</sub> O <sub>2</sub>	326	1864	3860	4527	2830	12404	S
<i>n</i> -Docosanoic acid	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	340	13124	18687	18250	7541	85295	S
<i>n</i> -Tricosanoic acid	C <sub>23</sub> H <sub>46</sub> O <sub>2</sub>	354	2606	8069	5256	2342	12482	S
<i>n</i> -Tetracosanoic acid	C <sub>24</sub> H <sub>48</sub> O <sub>2</sub>	368	14531	16789	14605	2072	47050	S
<i>n</i> -Pentacosanoic acid	C <sub>25</sub> H <sub>50</sub> O <sub>2</sub>	382	1321	4541	323	2843	8160	S
<i>n</i> -Hexacosanoic acid	C <sub>26</sub> H <sub>52</sub> O <sub>2</sub>	396	10061	5749	10840	1935	55648	S
<i>n</i> -Heptacosanoic acid	C <sub>27</sub> H <sub>54</sub> O <sub>2</sub>	410	191	2543	1041	1722	12314	S
<i>n</i> -Octacosanoic acid	C <sub>28</sub> H <sub>56</sub> O <sub>2</sub>	424	1535	16206	11671	3275	146571	S
<i>n</i> -Nonacosanoic acid	C <sub>29</sub> H <sub>58</sub> O <sub>2</sub>	438		2683	1086		9592	S
<i>n</i> -Triacontanoic acid	C <sub>30</sub> H <sub>60</sub> O <sub>2</sub>	452	574	15797	3522		21681	S
<i>n</i> -Hentriacontanoic acid	C <sub>31</sub> H <sub>62</sub> O <sub>2</sub>	466		1158				S
<i>n</i> -Dotriacontanoic acid	C <sub>32</sub> H <sub>64</sub> O <sub>2</sub>	480		2359			2217	S
<i>n</i> -Hexadecenoic acid	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	268	2351			44921	4023	S
<i>n</i> -Octadecadienoic acid	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	280	1664					S
<i>n</i> -Octadecenoic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	282	5164			9769	7894	S
$\alpha,\omega$ -Nonanedioic acid	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub>	188		427			641	S
$\alpha,\omega$ -Hexadecanedioic acid	C <sub>16</sub> H <sub>30</sub> O <sub>4</sub>	286	98	293	232	1292	629	A
$\alpha,\omega$ -Octadecanedioic acid	C <sub>18</sub> H <sub>34</sub> O <sub>4</sub>	314			82	977	505	S
$\alpha,\omega$ -Eicosanedioic acid	C <sub>20</sub> H <sub>38</sub> O <sub>4</sub>	342				473	308	S
$\alpha,\omega$ -Docosanedioic acid	C <sub>22</sub> H <sub>42</sub> O <sub>4</sub>	370				429	239	S
6-(2'-Hexylphenyl)heptanoic acid	C <sub>18</sub> H <sub>28</sub> O <sub>2</sub>	276					1605	S
7-(2'-Pentylphenyl)heptanoic acid	C <sub>18</sub> H <sub>28</sub> O <sub>2</sub>	276					1790	S
9-(2'-Propylphenyl)nonanoic acid	C <sub>18</sub> H <sub>28</sub> O <sub>2</sub>	276		9531			1481	S
10-(2'-Ethylphenyl)decanoic acid	C <sub>18</sub> H <sub>28</sub> O <sub>2</sub>	276					1554	S
11-(2'-Methylphenyl)undecanoic acid	C <sub>18</sub> H <sub>28</sub> O <sub>2</sub>	276	1762				1466	S
9-Oxo-octadecanoic acid	C <sub>18</sub> H <sub>34</sub> O <sub>3</sub>	298		13905				S
7-Phenylheptanoic acid	C <sub>13</sub> H <sub>18</sub> O <sub>2</sub>	206		1974	537			I
8-Phenyl octanoic acid	C <sub>14</sub> H <sub>20</sub> O <sub>2</sub>	220		3638	564			I
Total carboxylic acids			94718	317832	172314	254914	754719	
CPI			7.3	6.1	6.2	5.1	8.7	
Cmax			16	16	16	16	16	
<i>n-Alkanones</i>								
<i>(Natural products)</i>								
<i>n</i> -Hexadecan-2-one	C <sub>16</sub> H <sub>32</sub> O	240					3567	S
<i>n</i> -Heptadecan-2-one	C <sub>17</sub> H <sub>34</sub> O	254		2481	209		2164	S
<i>n</i> -Octadecan-2-one	C <sub>18</sub> H <sub>36</sub> O	268		3115			796	S
<i>n</i> -Nonadecan-2-one	C <sub>19</sub> H <sub>38</sub> O	282		6784	210		2303	S
<i>n</i> -Eicosan-2-one	C <sub>20</sub> H <sub>40</sub> O	296		931			551	S
<i>n</i> -Heneicosan-2-one	C <sub>21</sub> H <sub>42</sub> O	310		1861	274		4578	S
<i>n</i> -Docosan-2-one	C <sub>22</sub> H <sub>44</sub> O	324		1024	44		778	S
<i>n</i> -Tricosan-2-one	C <sub>23</sub> H <sub>46</sub> O	338		2140	296	2638	2205	S
<i>n</i> -Tetracosan-2-one	C <sub>24</sub> H <sub>48</sub> O	352		1117	93	1593	1122	S
<i>n</i> -Pentacosan-2-one	C <sub>25</sub> H <sub>50</sub> O	366	72	1163	194	1063	371	S

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Table 2 (continued)

Compound name	Composition	M.W.	Eucalyptus	Oregon Maple	Red Alder	Silver Birch	Dwarf Birch	ID Basis <sup>b</sup>
<i>n</i> -Hexacosan-2-one	C <sub>26</sub> H <sub>52</sub> O	380		1070	170	384	1367	S
<i>n</i> -Heptacosan-2-one	C <sub>27</sub> H <sub>54</sub> O	394	233	2053	308	486	5417	S
<i>n</i> -Octacosan-2-one	C <sub>28</sub> H <sub>56</sub> O	408		1048	32	618	1584	S
<i>n</i> -Nonacosan-2-one	C <sub>29</sub> H <sub>58</sub> O	422		2056	303	11782	21543	S
<i>n</i> -Triacontan-2-one	C <sub>30</sub> H <sub>60</sub> O	436		388		210	964	S
<i>n</i> -Hentriacontan-2-one	C <sub>31</sub> H <sub>62</sub> O	450		2915		657	2398	S
<i>n</i> -Dotriacontan-2-one	C <sub>32</sub> H <sub>64</sub> O	464		76				S
<i>n</i> -Tritriacontan-2-one	C <sub>33</sub> H <sub>66</sub> O	478		756			166	S
6,10,14-Trimethyl- pentadecan-2-one	C <sub>18</sub> H <sub>36</sub> O	268		5903	435	3041	1527	S
Total alkanones			305	36880	2568	22473	53399	
CPI			nd	2.5	5.3	5.9	3.8	
Cmax			27	19	27	29	29	
<i>n-Alkanols</i>								
<i>(Natural products)</i>								
<i>n</i> -Heneicosanol	C <sub>21</sub> H <sub>44</sub> O	312	57					S
<i>n</i> -Docosanol	C <sub>22</sub> H <sub>46</sub> O	326	363					A
<i>n</i> -Tricosanol	C <sub>23</sub> H <sub>48</sub> O	340	41					S
<i>n</i> -Tetracosanol	C <sub>24</sub> H <sub>50</sub> O	354	520	424		708		S
<i>n</i> -Pentacosanol	C <sub>25</sub> H <sub>52</sub> O	368	35			47		S
<i>n</i> -Hexacosanol	C <sub>26</sub> H <sub>54</sub> O	382	399	1115		95		S
<i>n</i> -Heptacosanol	C <sub>27</sub> H <sub>56</sub> O	396		15		95		S
<i>n</i> -Octacosanol	C <sub>28</sub> H <sub>58</sub> O	410	163	3845				S
<i>n</i> -Triacontanol	C <sub>30</sub> H <sub>62</sub> O	438		3574				S
Total <i>n</i> -alkanols			1579	5399		946		
CPI			18	> 50	nd	nd	nd	
Cmax			24	28	nd	24	nd	
<i>n-Alkylcyclohexanes</i>								
<i>(Alteration products)</i>								
<i>n</i> -Octylcyclohexane	C <sub>14</sub> H <sub>28</sub>	196			380			I
<i>n</i> -Decylcyclohexane	C <sub>16</sub> H <sub>32</sub>	224			268			I
<i>n</i> -Dodecylcyclohexane	C <sub>18</sub> H <sub>36</sub>	252		116	255			I
<i>n</i> -Octadecylcyclohexane	C <sub>24</sub> H <sub>48</sub>	336			3841			I
<i>n</i> -Eicosanylcyclohexane	C <sub>26</sub> H <sub>52</sub>	364		488	4683			I
<i>n</i> -Docosanylcyclohexane	C <sub>28</sub> H <sub>56</sub>	392		987				I
<i>n</i> -Tetracosanylcyclohexane	C <sub>30</sub> H <sub>60</sub>	420		906				I
<i>n</i> -Hexacosanylcyclohexane	C <sub>32</sub> H <sub>64</sub>	448		844				I
Total alkylcyclohexanes				3340	9426			
<i>n-Alkylbenzenes</i>								
<i>(Alteration products)</i>								
Docosanylbenzene	C <sub>28</sub> H <sub>50</sub>	386					245	I
<i>Wax esters</i>								
<i>(Natural products)</i>								
Heptadecyl hexadecanoate	C <sub>33</sub> H <sub>66</sub> O <sub>2</sub>	494				4450		I
<i>n-Alkylnitriles</i>								
<i>(Alteration products)</i>								
Hexadecanenitrile	C <sub>16</sub> H <sub>31</sub> N	237					1811	S
Octadecanenitrile	C <sub>18</sub> H <sub>35</sub> N	265					241	S
Eicosanenitrile	C <sub>20</sub> H <sub>39</sub> N	293					161	S
Docosanenitrile	C <sub>22</sub> H <sub>43</sub> N	321					174	S
Tricosanenitrile	C <sub>23</sub> H <sub>45</sub> N	335					77	S
Tetracosanenitrile	C <sub>24</sub> H <sub>47</sub> N	349					112	S

(continued on next page)

Table 2 (continued)

Compound name	Composition	M.W.	Eucalyptus	Oregon Maple	Red Alder	Silver Birch	Dwarf Birch	ID Basis <sup>b</sup>
Hexacosanenitrile	C <sub>26</sub> H <sub>51</sub> N	377					168	S
Octacosanenitrile	C <sub>28</sub> H <sub>55</sub> N	405					335	S
<i>II. Biomarkers</i>								
<i>Sesquiterpenoids (C<sub>15</sub>)</i>								
<i>(Alteration products)</i>								
cis-Thujan-10-oic acid	C <sub>10</sub> H <sub>16</sub> O <sub>2</sub>	168	981					I
Caryophylla-2(12),5-dien-13-aldehyde	C <sub>15</sub> H <sub>22</sub> O	218				3815		I
Sesquiterpanol	C <sub>15</sub> H <sub>26</sub> O <sub>2</sub>	238				40439		I
Geigerone	C <sub>15</sub> H <sub>18</sub> O <sub>4</sub>	262				4968		I
<i>Diterpenoids (C<sub>20</sub>)</i>								
<i>(Alteration products)</i>								
Dihydroretene	C <sub>18</sub> H <sub>20</sub>	236			1616			I
19-Norabieta-4(18),8,11,13-tetraene	C <sub>19</sub> H <sub>26</sub>	254	653					I
<i>Triterpenoids (C<sub>30</sub>)</i>								
<i>(Natural products)</i>								
Allobetul-2-ene	C <sub>30</sub> H <sub>48</sub> O	424				952		I
α-Amyrin	C <sub>30</sub> H <sub>50</sub> O	426		412				I
β-Amyrin	C <sub>30</sub> H <sub>50</sub> O	426		1235	743			I
3α-Lupeol	C <sub>30</sub> H <sub>50</sub> O	426		851	4829			I
3β-Lupeol	C <sub>30</sub> H <sub>50</sub> O	426			1497			I
<i>(Alteration products)</i>								
Des-A-allobetulin	C <sub>24</sub> H <sub>38</sub> O	342					6046	I
Nortriterpene	C <sub>29</sub> H <sub>48</sub>	396					1536	I
Triterpadiene	C <sub>30</sub> H <sub>46</sub>	406			238		813	I
Lupa-2,22(29)-diene	C <sub>30</sub> H <sub>48</sub>	408	787	904		4379		I
Oleana-2,12-diene	C <sub>30</sub> H <sub>48</sub>	408	552	760	705			I
Ursa-2,20-diene	C <sub>30</sub> H <sub>48</sub>	408		2451				I
Nortriterpenone	C <sub>29</sub> H <sub>46</sub> O	410					4173	I
Lupa-1,22(29)-dien-3-one	C <sub>30</sub> H <sub>46</sub> O	422		619				I
Lupa-2,22(29)-dien-28-al	C <sub>30</sub> H <sub>46</sub> O	422	175					I
α-Amyrone	C <sub>30</sub> H <sub>48</sub> O	424		35				I
β-Amyrone	C <sub>30</sub> H <sub>48</sub> O	424		285	349			I
Glutin-5-en-3-one	C <sub>30</sub> H <sub>48</sub> O	424			9269			I
Lupa-2,22(29)-dien-28-ol	C <sub>30</sub> H <sub>48</sub> O	424		634		1132		I
Lupenone	C <sub>30</sub> H <sub>48</sub> O	424	534	271	1487			I
Olean-13(18)-en-3-one	C <sub>30</sub> H <sub>48</sub> O	424			3726			I
Taraxerone	C <sub>30</sub> H <sub>48</sub> O	424			1260			I
Isomultifluorenone	C <sub>30</sub> H <sub>48</sub> O	424			1748			I
24-Norolean-2,12-en-28-oic acid	C <sub>29</sub> H <sub>46</sub> O <sub>2</sub>	426	325					I
24-Norursana-2,12-dien-28-oic acid	C <sub>29</sub> H <sub>46</sub> O <sub>2</sub>	426					3157	I
Lupa-2,22(29)-dien-28-oic acid	C <sub>30</sub> H <sub>46</sub> O <sub>2</sub>	438	849			34289		I
3-Methoxylupa-2,22(29)-diene	C <sub>31</sub> H <sub>50</sub> O	438			2764			I
Oleana-2,12-dien-18-oic acid	C <sub>30</sub> H <sub>46</sub> O <sub>2</sub>	438	5948			455	3012	I
Oleana-2,12-dien-28-oic acid	C <sub>30</sub> H <sub>46</sub> O <sub>2</sub>	438	3052					I
Ursana-2,12-dien-28-oic acid	C <sub>30</sub> H <sub>46</sub> O <sub>2</sub>	438	5240					I
Dihydronyctanthanoic acid	C <sub>30</sub> H <sub>50</sub> O <sub>2</sub>	442			1777			I
Olean-13(18)-en-3-on-28-oic acid	C <sub>31</sub> H <sub>48</sub> O <sub>3</sub>	454			604			I
29-Chlorolup-1-en-3-one	C <sub>30</sub> H <sub>47</sub> ClO	458			1428			I
Total triterpenoids			17462	8456	32425	41208	18737	

(continued on next page)

Table 2 (continued)

Compound name	Composition	M.W.	Eucalyptus	Oregon Maple	Red Alder	Silver Birch	Dwarf Birch	ID Basis <sup>b</sup>
<i>Steroids</i>								
<i>(Natural products)</i>								
Campesterol	C <sub>28</sub> H <sub>48</sub> O	400		271				I
Stigmasterol	C <sub>29</sub> H <sub>48</sub> O	412		674	1260			I
β-Sitosterol	C <sub>29</sub> H <sub>50</sub> O	414	254	3339	1821	2528	2187	I
<i>(Alteration products)</i>								
24-Ethyl-19-norcholesta-1,3,5(10),6,8,14-hexaene	C <sub>28</sub> H <sub>38</sub>	374				1212	384	I
24-Ethyl-19-norcholesta-1,3,5(10),6,8-pentaene	C <sub>28</sub> H <sub>40</sub>	376				846	430	I
24-Ethyl-19-norcholesta-1,3,5(10),8-tetraene	C <sub>28</sub> H <sub>42</sub>	378				254		I
24-Ethyl-14β(H)-1(10-6)-abeo-cholesta-5,7,9-triene	C <sub>29</sub> H <sub>46</sub>	394			228		398	I
24-Ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene	C <sub>29</sub> H <sub>46</sub>	394	336		202	3159	1035	I
Stigmasta-3,5-diene	C <sub>29</sub> H <sub>48</sub>	396				1662		I
Stigmasta-4,6-diene	C <sub>29</sub> H <sub>48</sub>	396				104		I
24-Ethylcholesta-4,22-diene	C <sub>29</sub> H <sub>46</sub>	396				254		I
Stigmast-5-ene	C <sub>29</sub> H <sub>50</sub>	398				6338	145	I
Stigmasta-3,5-dien-7-one	C <sub>29</sub> H <sub>46</sub>	410					1665	I
Total steroids			590	4284	3512	16357	6243	
<i>III. Polycyclic aromatic hydrocarbons (PAH)</i>								
<i>(Alteration products)</i>								
Fluorene	C <sub>13</sub> H <sub>10</sub>	166		1100				A
C <sub>1</sub> -Fluorenes	C <sub>14</sub> H <sub>12</sub>	180						I
Anthracene	C <sub>14</sub> H <sub>10</sub>	178				1302		A
Phenanthrene	C <sub>14</sub> H <sub>10</sub>	178	364	7741	2012	1606	1496	A
4(H)-Cyclopenta[def]phenanthrene	C <sub>15</sub> H <sub>10</sub>	190		1093				A
C <sub>1</sub> -Anthracenes/phenanthrenes	C <sub>15</sub> H <sub>12</sub>	192	345	3956	1972	1857	2233	I
Fluoranthene	C <sub>16</sub> H <sub>10</sub>	202	153	4203	2351	2669	822	A
Pyrene	C <sub>16</sub> H <sub>10</sub>	202	259	947	2352	984	3067	A
C <sub>2</sub> -Anthracenes/phenanthrenes	C <sub>16</sub> H <sub>14</sub>	206	121	1953	3914	1108	806	A
11(H)-Benzo[a]fluorene	C <sub>17</sub> H <sub>12</sub>	216		362	1083	293		A
11(H)-Benzo[b]fluorene	C <sub>17</sub> H <sub>12</sub>	216		291	2664	192		A
C <sub>1</sub> -Pyrenes	C <sub>17</sub> H <sub>12</sub>	216		1242		675		I
C <sub>3</sub> -Anthracenes/phenanthrenes	C <sub>17</sub> H <sub>16</sub>	220	103	118			1873	A
Benzo[ghi]fluoranthene	C <sub>18</sub> H <sub>10</sub>	226		979	4527	823		A
Benz[a]anthracene	C <sub>18</sub> H <sub>12</sub>	228		793	965	211		A
Chrysene	C <sub>18</sub> H <sub>12</sub>	228			1116	147		A
C <sub>4</sub> -Anthracenes/phenanthrenes	C <sub>18</sub> H <sub>18</sub>	234					1641	A
C <sub>1</sub> -Chrysenes	C <sub>19</sub> H <sub>14</sub>	242		209				A
Benzo[a]pyrene	C <sub>20</sub> H <sub>12</sub>	252		467	3225	147		A
3,3,7-Trimethyl-1,2,3,4-tetrahydrochrysene	C <sub>21</sub> H <sub>22</sub>	274	36					I
Total PAH			1726	31952	3225	14548	14172	
<i>IV. Phenols (lignin pyrolysis)</i>								
<i>(Natural products)</i>								
Cinnamic acid	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>	148			372			A
Coumaric acid	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	164	1713					A
Eugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	164				10991		A
α-Tocopherol	C <sub>29</sub> H <sub>50</sub> O <sub>2</sub>	430		1903				I

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Table 2 (continued)

Compound name	Composition	M.W.	Eucalyptus	Oregon Maple	Red Alder	Silver Birch	Dwarf Birch	ID Basis <sup>b</sup>
<i>(Alteration products)</i>								
Catechol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	110				27440	9493	I
Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	122			1341			I
Guaiacol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	124		1398				I
3-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	138			423			I
3,4-Dihydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>4</sub>	154	101					I
3,5-Dimethylphenol	C <sub>8</sub> H <sub>10</sub> O	122		770				I
3,5-Dimethoxy-4-hydroxytoluene	C <sub>9</sub> H <sub>12</sub> O <sub>3</sub>	168		17884				I
3,4-(Methylenedioxy)-5-methoxybenzaldehyde	C <sub>9</sub> H <sub>8</sub> O <sub>4</sub>	180						I
4,4'-Dimethyl-1,1'-biphenyl-	C <sub>14</sub> H <sub>14</sub>	182		682				I
Vanillin	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	152		9055				A
2,6-Dimethoxyphenol	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	154	377	36097		23817		I
Acetovanillone	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	166	62	5762	743			I
Vanillic acid	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	168	57	4547	1225	1775	3393	A
Pyrogallol	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	170				1022	5006	I
Guaiacylacetone	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	180	88					I
Homovanillyl alcohol	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	182	48	16123	1602	2903	2951	I
Acetosyringone	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	196	278	5692	1530			I
Homovanillic acid	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	196	79				3921	A
Syringic acid	C <sub>9</sub> H <sub>10</sub> O <sub>5</sub>	198	86	2089	732			I
3,5-Dimethoxy-4-coumaraldehyde	C <sub>11</sub> H <sub>12</sub> O <sub>4</sub>	208	1125		655			I
Syringylacetone	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub>	210	589	3616	869			I
Syringylpropanal	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub>	210	61					I
2,3,5-Trimethoxybenzoic acid	C <sub>10</sub> H <sub>12</sub> O <sub>5</sub>	212		655				I
3,5-Dimethoxy-4-coumaric acid	C <sub>11</sub> H <sub>12</sub> O <sub>5</sub>	224		5148				I
3,3'-Dimethoxy-4,4'-dihydroxystilbene	C <sub>16</sub> H <sub>16</sub> O <sub>4</sub>	272		5649				I
Divanillyl	C <sub>16</sub> H <sub>16</sub> O <sub>4</sub>	274	43		1006			I
Syringylvanillylmethane	C <sub>17</sub> H <sub>20</sub> O <sub>5</sub>	304	28					I
Disyringyl	C <sub>18</sub> H <sub>22</sub> O <sub>6</sub>	334	364		788			I
Tetrahydro-3,4-divanillylfuran	C <sub>20</sub> H <sub>24</sub> O <sub>5</sub>	344		2071	781	1236	1249	I
Total phenols			5099	119141	12068	69184	26012	
Syringyl skeletons/ vanillyl skeletons (S/V)			6.1	1.6	0.8	1.5	0.4	
<i>V. Monosaccharide derivatives</i>								
<i>(Alteration products)</i>								
Galactosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	162	231	7040	4041	7359	8101	A
Mannosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	162	154	5527	1172	3793	3429	A
Levogluconan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	162	30	18281	9785	23299	23213	A
Total monosaccharides			386	12567	5213	11153	11529	
<i>VI. Unknowns</i>								
						43134		
<i>VI. Miscellaneous</i>								
Unresolved complex mixture (mg/kg)			388	687129	211938	548937	462	
Unresolved:resolved (U:R) components			0.01	0.8	0.9	0.8	0.8	
Organic carbon per amount burned (mg/kg)			2051	25476	9926	19436	4260	
Elemental carbon (mg/kg)			219	595	368	1855	145	

(continued on next page)



Table 2 (continued)

Compound name	Composition	M.W.	Eucalyptus	Oregon Maple	Red Alder	Silver Birch	Dwarf Birch	ID Basis <sup>b</sup>
Organic carbon/elemental carbon (OC/EC)			9	43	27	10	29	
Methylphenanthrenes/phenanthrene (MP:P)			0.9	0.5	1.0	1.1	1.5	

<sup>a</sup> These data are also available from the corresponding author expressed as mg/g organic carbon (OC) emitted.

<sup>b</sup> Identification criteria: blank space indicates not present or below detection limit; nd = not determined. A = matches with authentic standard; S = interpolated from homologous series fragmentation pattern; I = interpreted from mass spectrum fragmentation pattern. All compositions and molecular weights are as the compounds occur in smoke (i.e. underivatized). CPI for *n*-alkanes, *n*-alkenes and *n*-alkanones:  $[CPI = \Sigma C_{13}-C_{35} / \Sigma C_{12}-C_{34}]$  from Mazurek and Simoneit (1984). CPI for *n*-alkanoic acids and *n*-alkanols:  $[CPI = \Sigma C_{12}-C_{34} / \Sigma C_{13}-C_{35}]$  from Mazurek and Simoneit (1984).

Mazurek and Simoneit, 1984) and to a minor degree from the *n*-alkanes by oxidation during incomplete combustion (Abas et al., 1995).

### 3.1.3. *n*-Alkanoic acids

The *n*-alkanoic acids range from C<sub>8</sub> to C<sub>32</sub>, show a strong even to odd C number predominance (CPI range from 5.1 to 8.7, average = 6.7), and a C<sub>max</sub> at 16 (Table 2, also Figs. 1d and 2d). These compounds, which are basic units of plant fats, oils and phospholipids, are identified here as the major compound class for deciduous tree smoke samples. There are also minor contributions from unsaturated fatty acids which include C<sub>16:1</sub>, C<sub>18:1</sub> and C<sub>18:2</sub> (Table 2).

### 3.1.4. $\alpha,\omega$ -Alkanedioic acids

A series of  $\alpha,\omega$ -alkanedioic acids is present and ranges from C<sub>16</sub> to C<sub>22</sub> (Table 2, also Figs. 1e, 2e, 4e and 5e). The most common  $\alpha,\omega$ -alkanedioic acid in deciduous tree smoke is C<sub>16</sub>. The photo-oxidation product of C<sub>18:1</sub> and C<sub>18:2</sub> alkenoic acids,  $\alpha,\omega$ -nonanedioic acid (Stephanou and Stratigakis, 1993), is also present, however, only in two samples. The  $\alpha,\omega$ -alkanedioic acids have been identified from a variety of sources and in the environment (Simoneit, 1989; Rogge et al., 1993; Hildemann et al., 1994; Abas et al., 1995; Gogou et al., 1996). High molecular weight  $\alpha,\omega$ -alkanedioic acids (C<sub>10</sub>–C<sub>24</sub>) have been identified in rural aerosol particles and their source may be oxidation products of  $\omega$ -hydroxyalkanoic acids from vegetation polyester biopolymers (Simoneit and Mazurek, 1982). The  $\alpha,\omega$ -alkanedioic acid homologous series indicate a general origin from lipid sources and are not specific for deciduous trees. The identification here of all acids confirms a source contribution from the burning of biomass.

### 3.1.5. *n*-Alkanones

The straight chain ketones as *n*-alkan-2-ones range from C<sub>16</sub> to C<sub>33</sub> and show an odd to even C number

predominance (CPI range from 2.5 to 5.9, average = 4.4) with various C<sub>max</sub> at 19, 27 and 29 (Table 2, also Figs. 3d, 4d and 5d). The *n*-alkan-2-ones are primarily derived from the partial combustion of aliphatic precursors (Simoneit, 1978).

### 3.1.6. *n*-Alkanols

Homologous series of *n*-alkanols with strong even to odd C number predominances are present in the smoke especially from burning of eucalyptus and maple (CPI = 18 and > 50). The *n*-alkanols ranged from C<sub>21</sub> to C<sub>30</sub> with C<sub>max</sub> at 24 and 28 (Table 2, also Figs. 1e–3e). The *n*-alkanols from C<sub>20</sub> to C<sub>30</sub> are predominantly of an epicuticular wax origin (Simoneit, 1978, 1989). The secondary alkanol, *n*-nonacosan-10-ol, found in all conifer smoke samples (Oros and Simoneit, 2001) was not detectable in these smoke emissions.

### 3.1.7. *n*-Alkyl nitriles

A series of *n*-alkyl nitriles ranging from C<sub>16</sub> to C<sub>28</sub> with a C<sub>max</sub> at 16 was identified only in smoke from Dwarf Birch (Fig. 5d). These compounds have not been reported previously in biomass burning extracts, however, they have been found in pyrolysates of kerogens (Derenne et al., 1993), in urban aerosols (Abas and Simoneit, 1996), in smoke from charbroiling and meat cooking operations (Rogge et al., 1991), and in smoke from burning of brown coal (Oros and Simoneit, 2000). The authors propose that the *n*-alkyl nitriles are formed by pyrolytic processes.

## 3.2. Molecular biomarkers

Molecular biomarkers (i.e. biomarkers) are organic compounds of a biological origin which show little or no change in chemical structure from their parent organic molecules (i.e. natural product) found in the living organism. Such molecules are characterized by their restricted occurrence, source specificity, molecular stability and suitable concentration for analytical detection

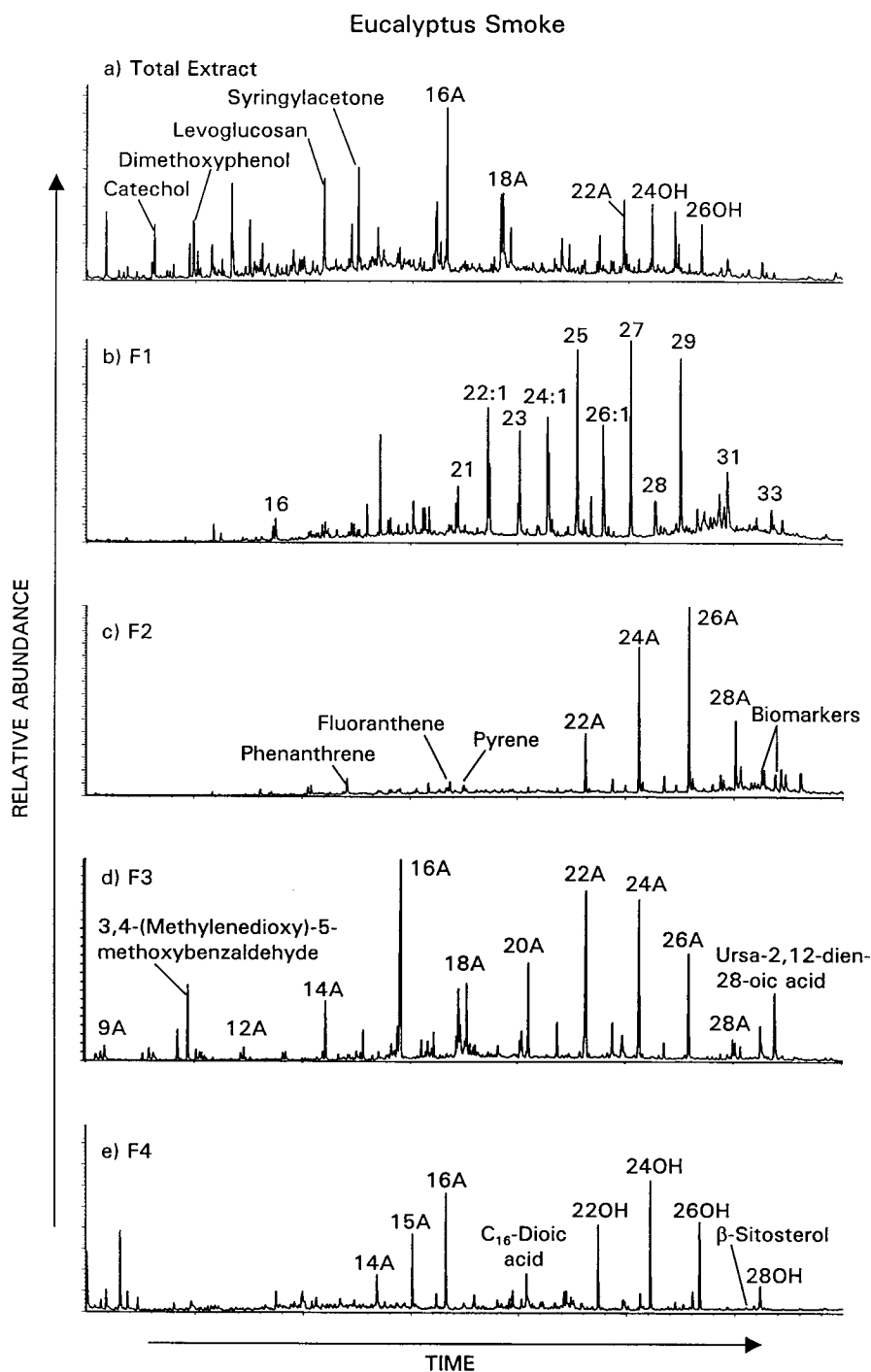


Fig. 1. GC–MS total ion current traces of Eucalyptus smoke particulate matter: (a) total extract showing the major organic components, (b) F1 fraction showing *n*-alkanes and *n*-alkenes, (c) F2 fraction showing *n*-alkanoic acids, PAH and triterpenoid biomarkers, (d) F3 fraction showing *n*-alkanoic acids, methoxyphenols and triterpenoid biomarkers, and (e) F4 fraction showing *n*-alkanoic acids, *n*-alkanols,  $\alpha,\omega$ -alkanedioic acids and steroid biomarkers (numbers refer to C chain length of *n*-alkanes, A = *n*-alkanoic acid, OH = *n*-alkanol).

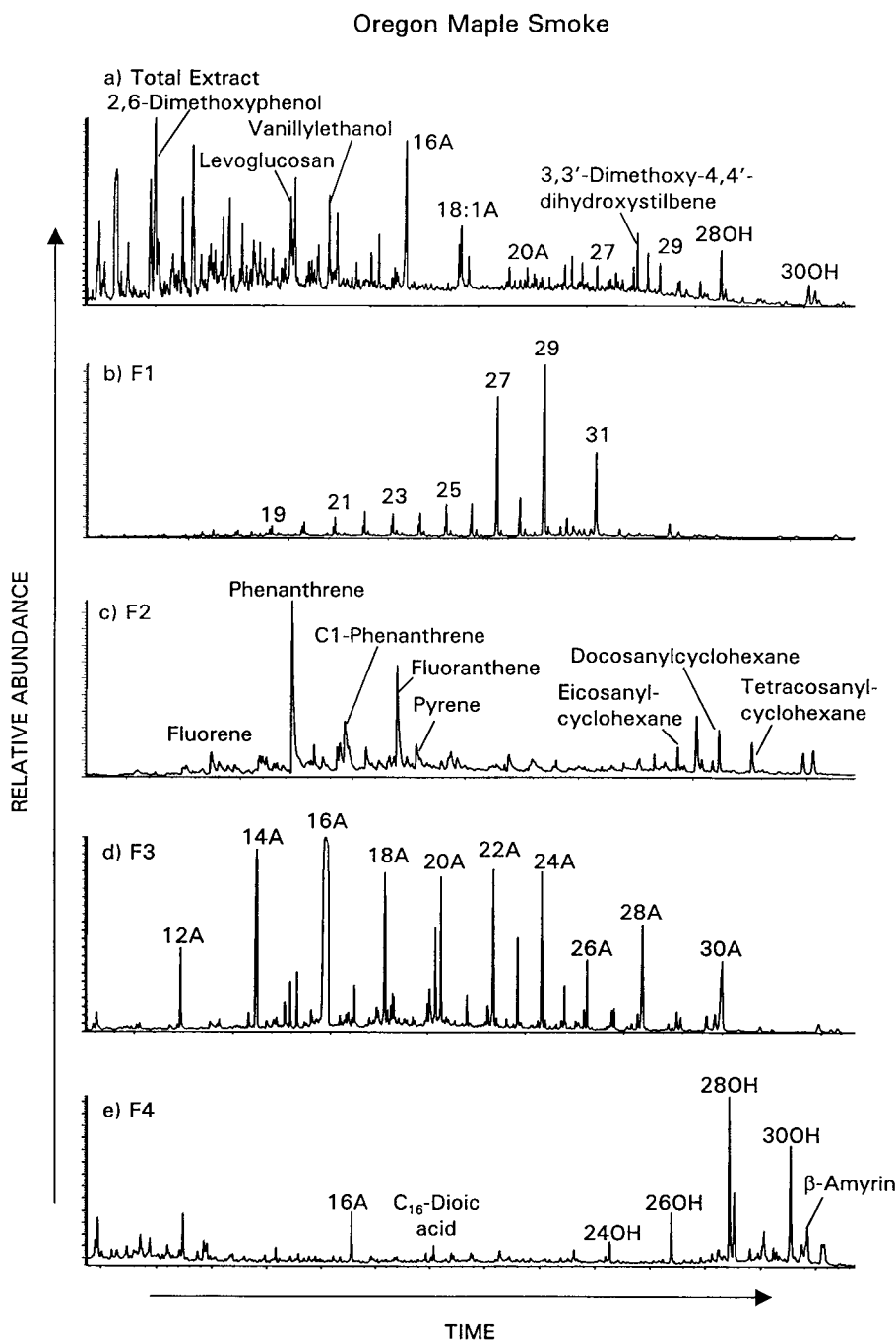


Fig. 2. GC-MS total ion current traces of Oregon Maple smoke particulate matter: (a) total extract showing the major organic components, (b) F1 fraction showing *n*-alkanes, (c) F2 fraction showing PAH and alkylcyclohexanes, (d) F3 fraction showing *n*-alkanoic acids, (e) F4 fraction showing *n*-alkanoic acids and *n*-alkanols (abbreviations as in Fig. 1).

(Mazurek and Simoneit, 1984, 1997). The major biomarkers identified in the deciduous tree smoke samples include triterpenoids, monosaccharide derivatives from cellulose, methoxyphenols from lignin, and sterols,

including their thermal alteration products. It has been shown that these high molecular weight compounds are volatilized directly into smoke by an injection mechanism similar to steam volatilization/stripping (Simoneit et

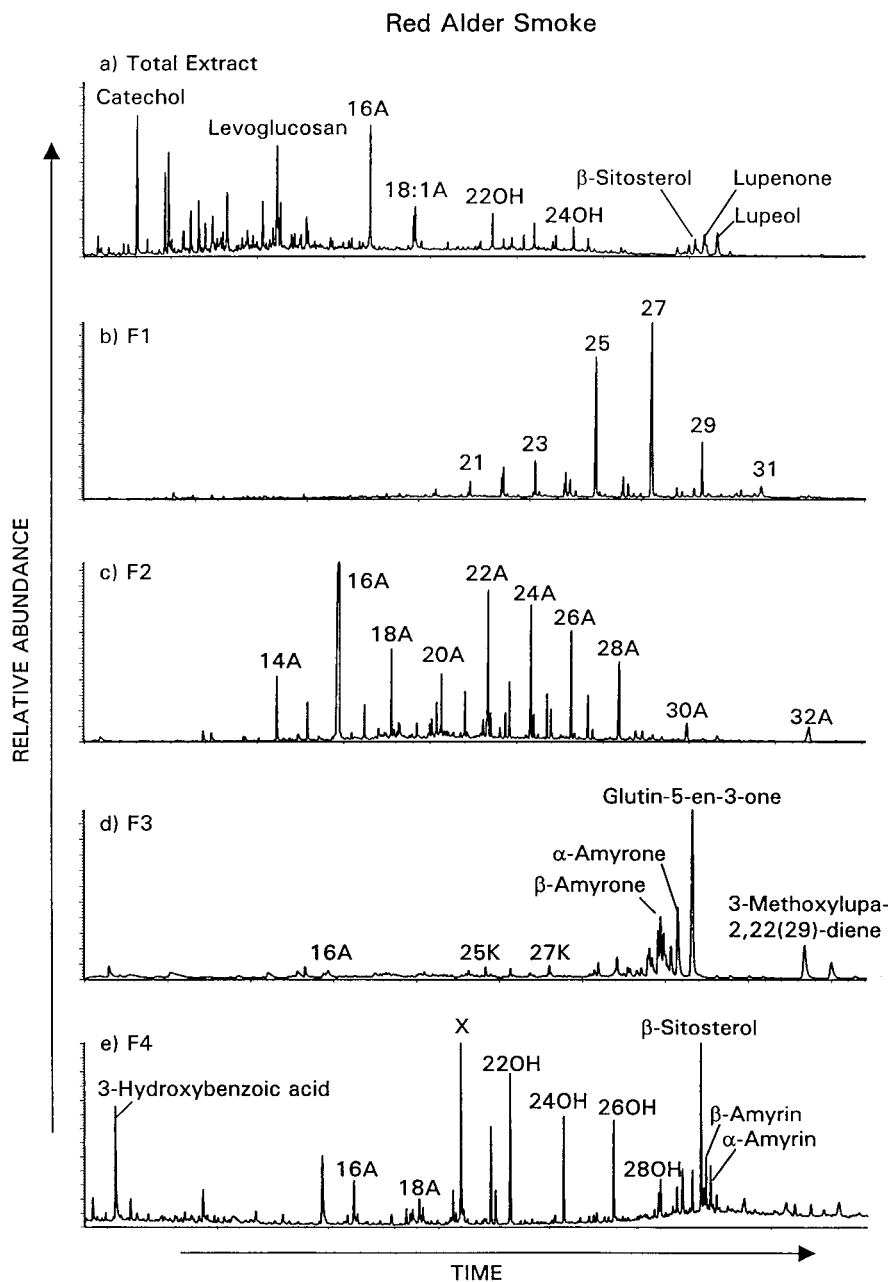


Fig. 3. GC-MS total ion current traces of Red Alder smoke particulate matter: (a) total extract showing the major organic components, (b) F1 fraction showing *n*-alkanes, (c) F2 fraction showing *n*-alkanoic acids, (d) F3 fraction showing *n*-alkanoic acids, *n*-alkanones and triterpenoid biomarkers, and (e) F4 fraction showing *n*-alkanoic acids, *n*-alkanols, methoxyphenols, steroids and triterpenoid biomarkers (abbreviations as in Fig. 1).

al., 1993; Abas et al., 1995). Subsequent condensation onto or entrapment into preexisting particulate matter, when the smoke plume is diluted and cooled, provides the means for the incorporation of these compounds into the atmospheric aerosol phase (Simoneit et al., 1993).

### 3.2.1. Triterpenoids

Triterpenoids are important biomarker constituents of many higher plants, especially of angiosperms, in their gums and mucilages (Deshmane and Dev, 1971; Jain and Seshadri, 1971; Ghosh et al., 1985; Hemmers et al., 1989; Koops et al., 1991; Williams et al., 1992;

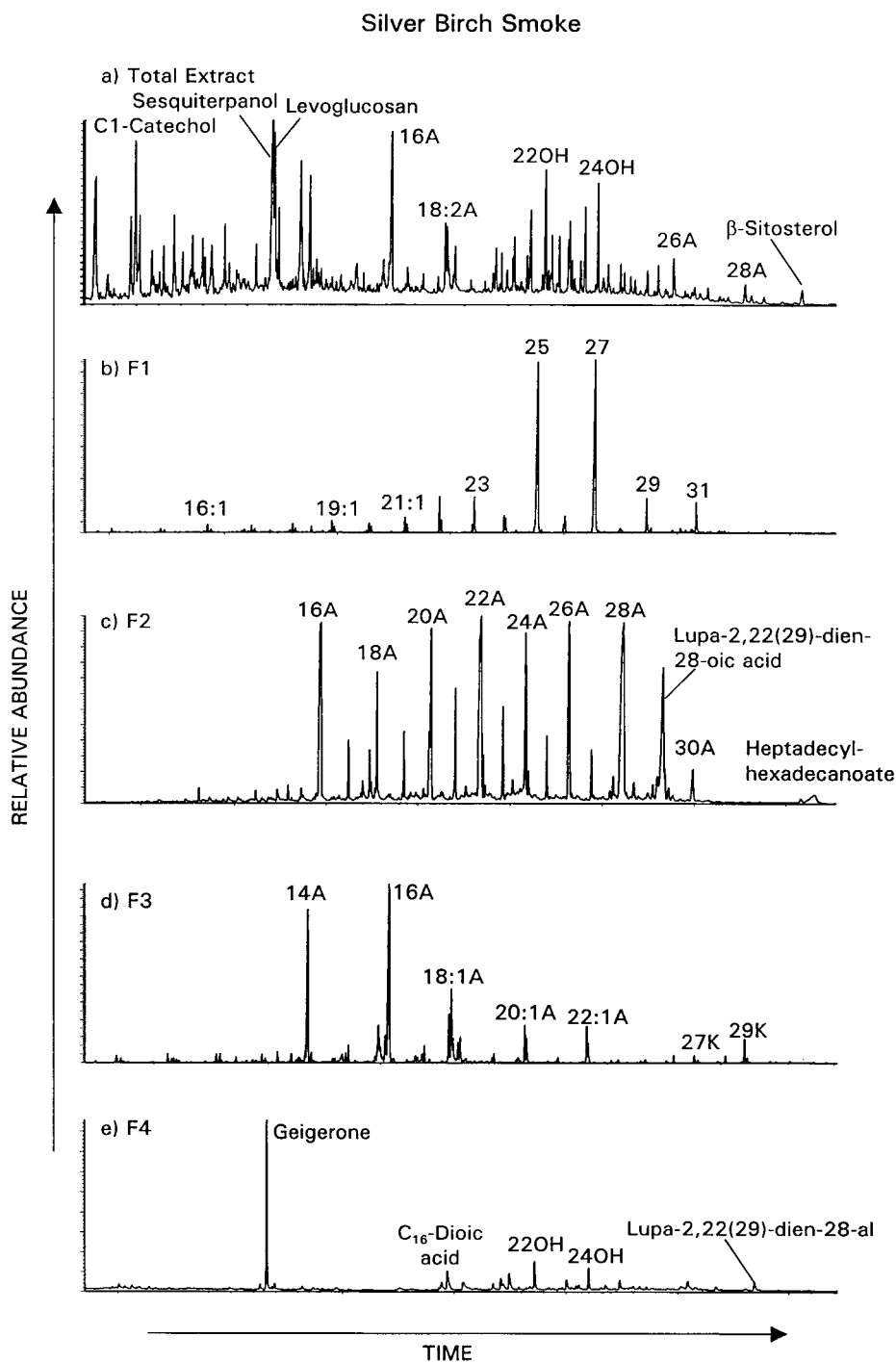


Fig. 4. GC-MS total ion current traces of Silver Birch smoke particulate matter: (a) total extract showing the major organic components, (b) F1 fraction showing *n*-alkanes and *n*-alkenes, (c) F2 fraction showing *n*-alkanoic acids, triterpenoid biomarkers and wax esters, (d) F3 fraction showing *n*-alkanoic acids and *n*-alkanones, (e) F4 fraction showing  $\alpha,\omega$ -alkanedioic acids, *n*-alkanols and triterpenoid biomarkers (abbreviations as in Fig. 1).

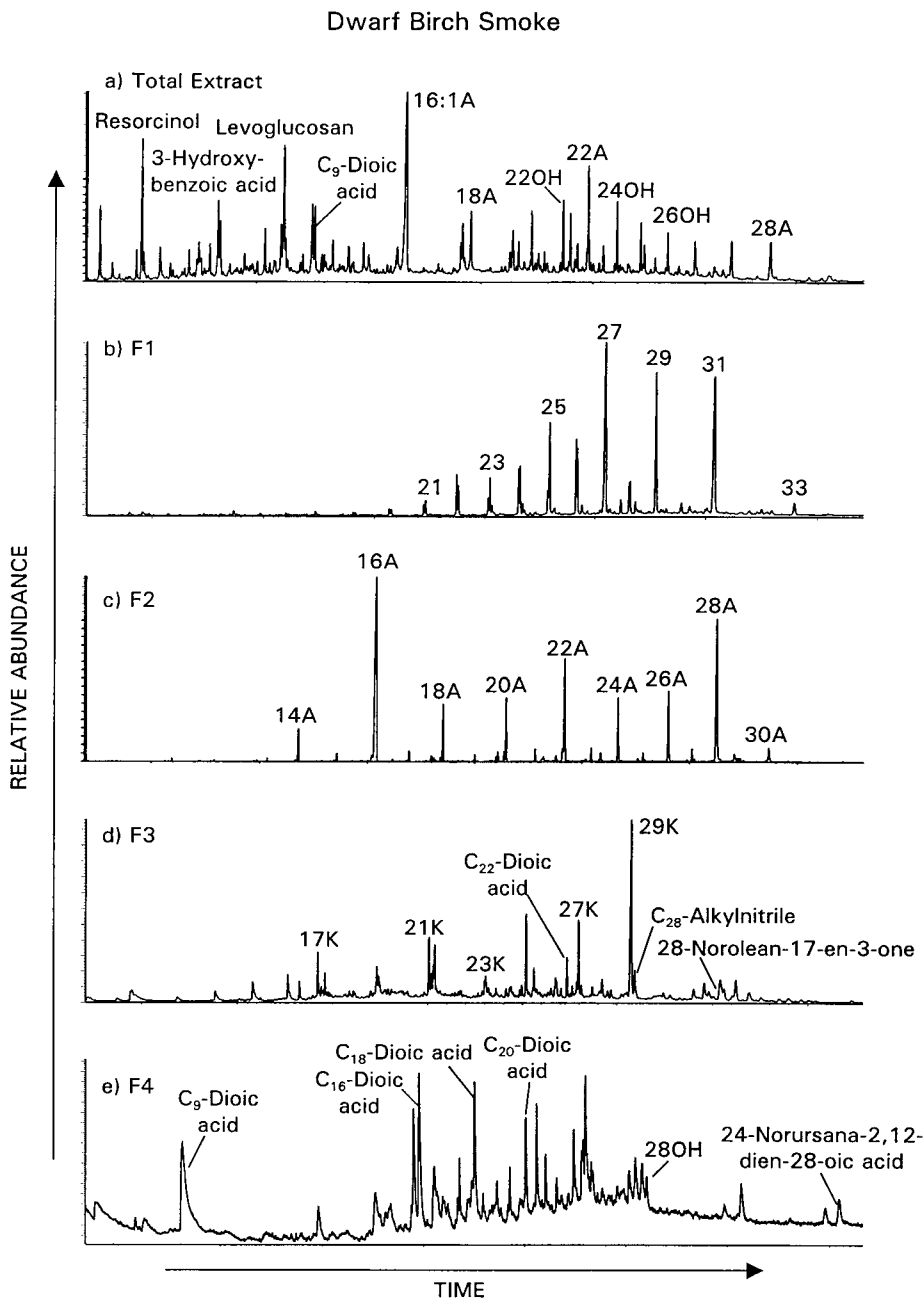


Fig. 5. GC-MS total ion current traces of Dwarf Birch smoke particulate matter: (a) total extract showing the major organic components, (b) F1 fraction showing *n*-alkanes, (c) F2 fraction showing *n*-alkanoic acids, (d) F3 fraction showing *n*-alkanones,  $\alpha,\omega$ -alkanedioic acids, *n*-alkynitriles and triterpenoid biomarkers, and (e) F4 fraction showing  $\alpha,\omega$ -alkanedioic acids, *n*-alkanols, and triterpenoid biomarkers (abbreviations as in Fig. 1).

Rickling and Glombitza, 1993). The predominant biomarkers identified in deciduous tree smoke are thermal alteration (oxidation) products with the lupane, oleanane and ursane skeletons. The most common triterpenoid alteration products present in the smoke samples include lupa-2,22-diene, oleana-2,12-diene, oleana-2,12-

dien-18-oic acid and  $\beta$ -amyrene (Table 2, also Fig. 3d and e). The product-precursor relationship for the triterpenoids in these smoke samples may follow an alteration pathway which commences with the dehydrogenation of oleanolic and ursolic acid precursors, major triterpenoids found in angiosperm gums and

mucilages, to dienes (Simoneit, 1998, Fig. 6). Subsequent dehydrogenation of triterpenoid precursors results in partial aromatic hydrocarbon derivatives as intermediate products. Further dehydration of these intermediates yields the aromatic biomarkers.

### 3.2.2. Steroids

The sterols, generally comprised of the C<sub>28</sub> and C<sub>29</sub> phytosterol compounds, are constituents of plant lipid membranes and waxes (Goad, 1977; Goodwin, 1980). The sterol biomarkers are present in all deciduous tree smoke samples analyzed (Table 2, also Figs. 1d, 3a and 3d). The natural product  $\beta$ -sitosterol is the most common sterol in deciduous tree smoke followed by stigmasterol and campesterol, also the natural products. Several C<sub>29</sub> thermal alteration products from the sterol precursor  $\beta$ -sitosterol are present and include stigmast-5-ene, stigmast-4,6-diene, stigmast-3,5-diene and stigmast-3,5-dien-7-one. Various aromatization products (e.g., 24-ethyl-19-norcholesta-1,3,5(10)-triene and 24-ethyl-19-norcholesta-1,3,5(10),6,8-pentaene, also see schematic showing sterol aromatization pathway cited as Fig. 7 in Oros and Simoneit, 2001) are also present and comprise a significant portion of the steroid content. The thermal alteration products of sterol precursors can be used as general indicators for burning of higher plant lipids (Simoneit, 1989; Simoneit et al., 1993). Overall, the phytosterols and their alteration products are present only as minor constituents in these smoke samples.

### 3.2.3. Monosaccharide derivatives

Cellulose and hemicellulose biopolymers which are mainly responsible for structural strength compose approximately 40–50% and 20–30% dry weight of wood, respectively (Sergejewa, 1959; Petterson, 1984). A cellulose molecule is a long-chain, linear polymer made up of 7000 to 12,000 D-glucose monomers, while a hemicellulose molecule is a 100–200 sugar monomer polysaccharide mixture of glucose, mannose, galactose, xylose, arabinose, 4-O-methylglucuronic acid and galacturonic acid (Sergejewa, 1959; Parham and Gray, 1984). It is the burning of wood at temperatures > 300°C which gives rise to the source specific molecular tracers, i.e. mainly 1,6-anhydro- $\beta$ -D-glucopyranose, also called levoglucosan, with lower amounts of galactosan and mannosan (Table 2, also Figs. 1a–5a). Levoglucosan has been previously reported in biomass burning smoke and atmospheric particles (Hornig et al., 1985; Locker, 1988; Simoneit et al., 1999; Oros and Simoneit, 2001). Levoglucosan is the predominant monosaccharide in smoke and is detectable as a major component in all samples analyzed. The levels of levoglucosan reported for these smoke samples are actually low due to extraction using only CH<sub>2</sub>Cl<sub>2</sub> (typically they are  $\times 10$  greater using a polar solvent). None-

theless, levoglucosan is emitted at high concentrations in smoke from deciduous fuel and is detectable in aerosol particulate matter at considerable distances from combustion sources (Simoneit et al., 1999).

### 3.2.4. Methoxyphenols

Lignin biopolymer comprises approximately 20–30% of the dry weight of wood (Sergejewa, 1959; Petterson, 1984). The lignin biopolymers are derived from p-coumaryl, coniferyl and sinapyl alcohols and contain mainly anisyl, vanillyl and syringyl nuclei (Simoneit et al., 1993). Deciduous tree lignin is enriched in the sinapyl alcohol precursor and on burning produces primarily syringyl and vanillyl moieties. Burning (pyrolysis) of wood injects these lignin nuclei into smoke as breakdown products such as acid, aldehyde, ketone and alkyl derivatives of the methoxyphenols (Hawthorne et al., 1988, 1989, 1992; Edye and Richards, 1991; Simoneit et al., 1993; Mazurek and Simoneit, 1997; Rogge et al., 1998).

The methoxyphenols and their thermal alteration products (Table 2) are significant biomarkers present in deciduous tree smoke. The methoxyphenols are composed mainly of lignin pyrolysis products, lignans and dimers of substituted phenols. The predominant phenolic biomarkers in deciduous tree smoke include 2,6-dimethoxyphenol, pyrogallol, homovanillyl alcohol, vanillic acid, vanillin, acetovanillone, syringic acid, acetosyringone, and syringyl acetone (Table 2, also Figs. 1a–5a). The phenolic compound guaiacylacetone is also found. Guaiacyl derivatives are potential biomarker tracers for both hard and softwoods (Hawthorne et al., 1988). A major lignan of deciduous tree smoke is tetrahydro-3,4-divanillylfuran (Table 2). Lignans have been described previously as tracers for distinguishing between coniferous and deciduous wood smoke emissions (Simoneit et al., 1993). Secondary products as dimers of substituted phenols are present and include divanillyl and disyringyl. They are derived from coniferyl and sinapyl alcohol type precursors and have been previously identified in wood smoke (Hawthorne et al., 1988; Simoneit et al., 1993). The lignin phenols, lignans and secondary dimers have mainly coniferyl and sinapyl alcohol type phenolic structures. Angiosperm lignin contains high proportions of the sinapyl as well as the coniferyl alcohol subunits, which are the precursors to the syringyl and guaiacyl degradation products from oxidation or pyrolysis (Hedges and Ertel, 1982). Hawthorne et al. (1989) and Simoneit et al. (1993) concluded that the syringyl moieties are indicators in smoke from burning of angiosperm fuels.

The ratios of the total natural and altered compounds that contain the syringyl skeleton to the total natural and altered compounds that contain the vanillyl skeleton (S/V, syringyl moieties/vanillyl moieties) range from

0.4 to 6.1 (average = 1.7) for these samples (Table 2). The S/V ratios are qualitatively distinct for each deciduous tree smoke sample. Thus, they may prove useful indicators of source specific burn emissions.

### 3.3. Polycyclic aromatic hydrocarbons

All biomass fires are pyrolysis processes causing the formation of polynuclear aromatic hydrocarbons (PAH) from (a) the high temperature thermal alteration of natural product precursors in the source organic matter and (b) the recombination of molecular fragments in the smoke (Simoneit, 1998). The identifications and abundances of over 20 PAH compounds present in the deciduous tree smoke samples are given in Table 2. The major PAH are phenanthrene, anthracene, C<sub>1</sub>-phenanthrenes (since anthracene is a minor PAH, the alkyl-anthracenes are expected to be negligible, based on compound elucidation for other combustion samples, Simoneit, 1998), fluoranthene and pyrene followed by lesser amounts of C<sub>2</sub>- and C<sub>3</sub>-phenanthrenes, C<sub>1</sub>-pyrenes, 11(H)-benzo[a]fluorene, and chrysene (see Figs. 1c and 2c). Certain PAH which exhibit mutagenic and genotoxic potential such as benz[a]anthracene and benzo[a]pyrene (Arcos and Argus, 1975; IARC, 1989), are also present, however only as minor constituents. The PAH identified here are also emitted by internal combustion engines, coal burning, and other anthropogenic sources (Rogge et al., 1993; Simoneit, 1998; Oros and Simoneit, 2000, 2001). They are thus not exclusive markers for biomass combustion.

The ratio of methylphenanthrenes to phenanthrene (MP:P) has been previously used as an indicator of anthropogenic influences in the environment: 0.5 for atmospheric fallout (Takada et al., 1991), 0.5–1.0 for combustion sources (Prahl and Carpenter, 1983), 1.0 for street and urban dusts (Takada et al., 1990, 1991), 2.0–6.0 for fossil fuel (Prahl and Carpenter, 1983), and 4.0 for crankcase oil (Pruel and Quinn, 1988). The range of the MP:P ratio determined for the deciduous tree smoke samples is 0.5–1.5 (average = 1.0). This value is smaller than the M:P ratio determined previously for conifer smoke (0.5–2.6, average = 1.6) (Oros and Simoneit, 2001), thus it may be used to distinguish between these two biomass fuel sources in smoke emissions.

### 3.4. Unresolved complex mixture

An unresolved complex mixture (UCM) of structurally complex isomers and homologs of branched and cyclic compounds (Eglinton et al., 1975) eluting as a hump typically between the C<sub>14</sub> and C<sub>34</sub> alkanes is present as an organic component of all total extracts from the smoke samples (Figs. 1a–5a). The UCM, which has been thoroughly examined in petroleum sources, is

comprised of compounds which are relatively inert to atmospheric or microbial degradation (Gough and Rowland, 1990; Killops and Al-Juboori, 1990). The ratio of UCM to resolved components (U:R) has been used as a parameter for the indication of petroleum contribution to aerosol particle samples (Mazurek and Simoneit, 1984). The U:R ratios for deciduous tree smoke samples were quantified in order to determine if this parameter is useful for distinguishing between angiosperm, gymnosperm (conifer) and fossil fuel derived combustion source emissions (Table 2). The deciduous tree smoke U:R ratios range from 0.01 to 0.9 (average = 0.7). Several U:R ratios have been determined from more mature fossil fuel derived combustion emission sources which include the following: lignite coal = 3.2 and bituminous coal = 3.3 (Oros and Simoneit, 2000); catalyst-equipped automobile engine exhaust = 5.5 and heavy-duty diesel truck engine exhaust = 9.3 (Rogge et al., 1993). Conifer smoke U:R ratios range from 0.6 to 1.4 (average = 1.0) (Oros and Simoneit, 2001). Thus, the lower U:R ratio of deciduous tree smoke shows that this parameter is useful for distinguishing between this biomass burning source and fossil fuel derived combustion source emissions. However, the close similarity in U:R ratios between deciduous tree and conifer smoke samples suggests that this parameter cannot be used to distinguish between these two biomass fuel sources in smoke emissions.

### 3.5. Organic and elemental carbon

The concentrations of organic C (OC) and elemental C (EC, i.e. black soot) in the deciduous tree smoke samples are given in Table 2. The organic to elemental C ratios (OC/EC) show a range from 9 to 43 (average = 23.6). The OC/EC ratios for the deciduous tree smoke samples are elevated in comparison to ambient air samples collected from rural sites (Crater Lake, OR = 12.4, Carus, OR = 6.5, and Sauvie, OR = 4.1) and urban areas (Los Angeles = 1.6, New York = 1.4, Santiago Chile = 1.7, China = 1.5) (Didyk et al., 2000). The low OC/EC ratios for mainly urban and suburban areas indicate a strong influence from petroleum derived combustion emissions. The deciduous tree smoke OC/EC ratios are much less than that measured from an ambient air sample collected at a remote area (South Atlantic Ocean = 160, Didyk et al., 2000) where influence from both petroleum combustion and biomass burning emissions is negligible. This distribution indicates that the OC/EC ratio measured for deciduous tree smoke may be useful in distinguishing this source from petroleum derived combustion emissions such as those found in rural and urban areas. However, the deciduous tree smoke OC/EC ratio is similar to the ratio determined previously for conifer smoke (3–78, average = 35; Oros and Simoneit, 2001), thus it cannot be used to



distinguish between these two biomass fuel sources in smoke emissions.

### 3.6. Major compound groups

The total emission factors (mg/kg) and % abundances of the major compound groups identified in deciduous wood smoke are given in Table 3. Of the total resolved components the major compound groups are the carboxylic acids (56.4%) from internal lipids, *n*-alkanes (15.1%) from waxes and methoxyphenols (8.4%) derived from lignin. Other compound groups such as triterpenoid and steroid biomarkers and aliphatic homologous series are present at low abundances (< 5%). Although wood is composed mostly of cellulose (40–50% of dry weight of wood, d.w.w.), with lesser amounts of hemicelluloses (20–30% of d.w.w.), and lignin (20–30% of d.w.w.) (Sergejewa, 1959; Petterson, 1984), the % abundance of the monosaccharide derivatives (1.5%) from cellulose alteration is less than the methoxyphenols. This observation is likely due to burning of the selected plant parts (leaves and branches of 1–2 cm thickness) which were relatively immature in plant structural development and to the lower solubility of the monosaccharide derivatives in the extraction solvent.

### 3.7. Major and unique biomarker tracers

The major biomarker compounds identified for smoke from deciduous trees to be applied as potential tracers in the atmosphere are given in Table 4. These are the methoxyphenolic compounds derived from lignin combustion which contain both coniferyl and sinapyl alcohol precursors. The methoxyphenolic biomarker

tracers include catechol, homovanillyl alcohol, vanillic acid, vanillin, acetovanillone, pyrogallol, homovanillic acid, syringic acid, syringyl acetone, acetosyringone and disyringyl. The syringyl moieties, typical of the sinapyl alcohol precursor in lignin biopolymer, are useful biomarker indicators for deciduous tree smoke emissions. The triterpenoid biomarker tracers are combustion alteration products which include oleana-2,12-dien-18-oic acid, lupa-2,22-diene, lupenone, oleana-2,12-diene, lupa-2,22(29)-dien-3-ol and  $\beta$ -amyrone (Fig. 6). The natural product  $\beta$ -amyrin is also present as a significant biomarker tracer. The dominant biomarker derived from combustion of cellulose biopolymer is levoglucosan, which has been previously proposed as a tracer for cellulose burning. Galactosan and mannosan are also detectable as secondary cellulose derivatives. The steroid biomarker tracers are the natural products  $\beta$ -sitosterol and campesterol, with minor thermally altered

Table 4  
Major biomarker tracers identified in deciduous tree smoke

Major biomarker tracer	Total emission factor (mg/kg) <sup>a</sup>	Abundance (%) <sup>b</sup>
<i>Methoxyphenols</i>		
Catechol	37±11	1.3
Homovanillyl alcohol	24±6	0.8
Vanillic acid	11±2	0.4
Vanillin	97±4	0.3
Acetosyringone	8±2	0.3
Acetovanillone	7±2	0.2
Pyrogallol	6±2	0.2
Tetrahydro-3,4-divanillylfuran	5±1	0.2
Syringylacetone	5±1	0.2
Homovanillic acid	4±2	0.1
Syringic acid	3±1	0.1
Disyringyl	1±0.3	0.1
<i>Triterpenoids</i>		
Olean-2,12-dien-18-oic acid	9±2	0.3
Lupa-2,22-diene	6±2	0.2
Lupenone	2±0.5	0.1
Oleana-2,12-diene	2±0.4	0.1
$\beta$ -Amyrin	2±0.5	0.1
Lupa-2,22(29)-dien-3-ol	2±0.5	0.1
$\beta$ -Amyrone	0.6±0.1	0.1
<i>Monosaccharide derivatives</i>		
Levoglucosan	75±11	2.6
Galactosan	27±4	0.9
Mannosan	14±2	0.5
<i>Steroids</i>		
$\beta$ -Sitosterol	10±1	0.4
Campesterol	0.3±0.1	0.1

<sup>a</sup> Sum and standard deviation for individual compounds listed in Table 2.

<sup>b</sup> % Abundance relative to total resolved organic components.

Table 3  
Major compound groups identified in deciduous tree smoke

Major compound group	Total emission factor (mg/kg) <sup>a</sup>	Abundance (%) <sup>b</sup>
Carboxylic acids	1589±258	56.4
<i>n</i> -Alkanes	425±73	15.1
Methoxyphenols	237±50	8.4
<i>n</i> -Alkenes	129±35	4.6
Triterpenoids	118±13	4.2
Alkanones	116±23	4.1
PAH	66±12	2.3
Monosaccharide derivatives	41±5	1.5
Steroids	31±6	1.1
Alkylcyclohexanes	13±4	0.5
<i>n</i> -Alkanols	8±2	0.3
Unknowns	43±19	1.5

<sup>a</sup> Sum and standard deviation of each compound group listed in Table 2.

<sup>b</sup> % Abundance relative to sum of total emission factors.

Table 5

Abundances (% relative to maximum) of key biomarkers for identifying fuel type

Sample	Heptacosane	Docosanoic acid	Levoglucosan	$\beta$ -Sitosterol	Vanillic acid	Syringic acid	Amyrins and derivatives	Betulin and derivatives
Eucalyptus	23	100	0.2	1.9	0.4	0.7	100	5
Oregon Maple	71	100	98	18	24	11	44	2
Red Alder	100	95	51	9	6	4	42	4
Silver Birch	100	12	36	4	3	0	0	64
Dwarf Birch	30	100	27	3	4	0	4	9

### Mechanisms of Triterpenoid Alteration

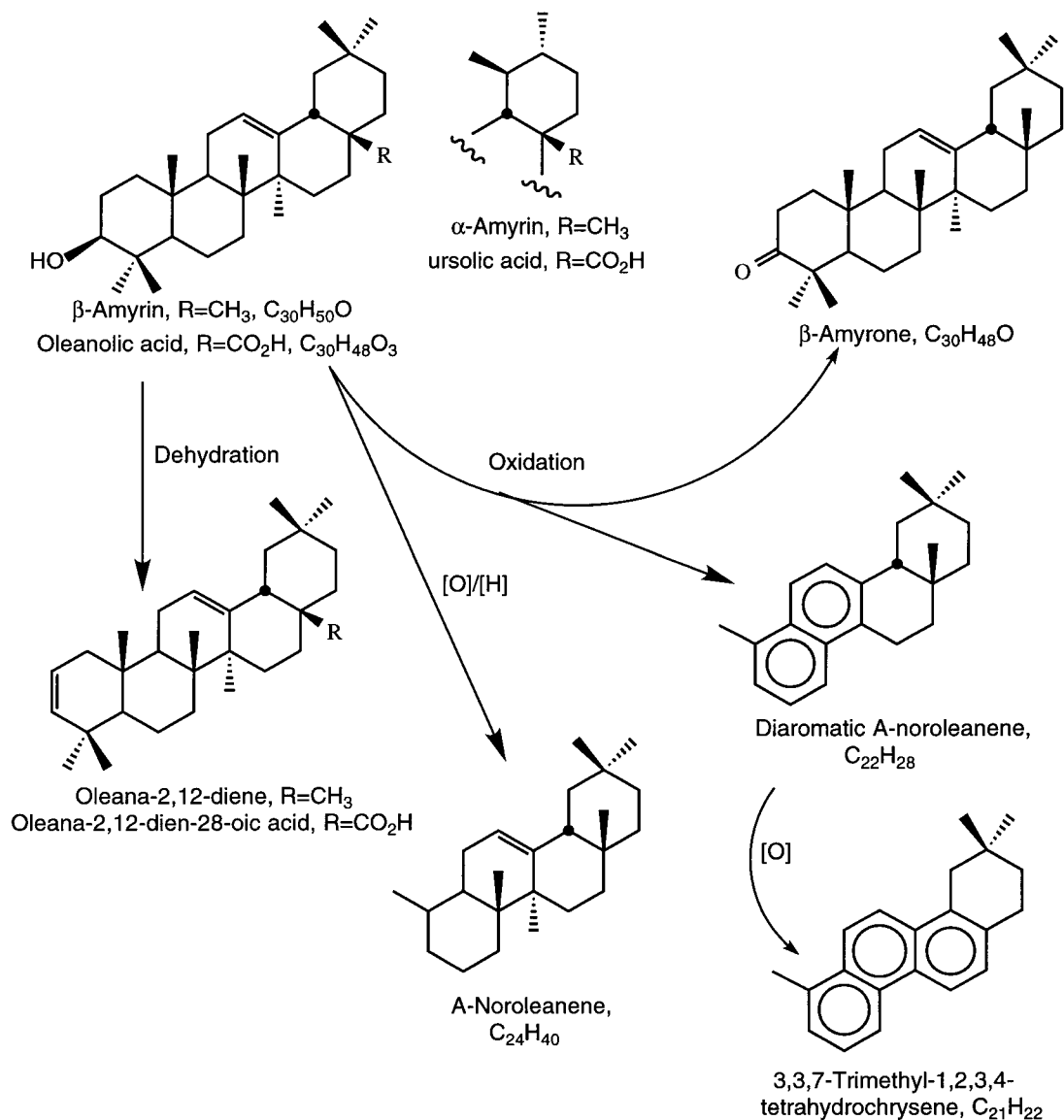


Fig. 6. The thermal alteration products of typical triterpenoid biomarker precursors observed in deciduous tree smoke samples (only major compounds are shown).

derivatives. Compound series such as *n*-alkanes, *n*-alkenes, *n*-alkanoic acids, *n*-alkanones, *n*-alkanols, PAH, phytosterols, anhydrosaccharides (e.g. levoglucosan), and UCM are not source specific, because they are generally found in all biomass combustion emissions (Simoneit, 1984, 1989; Abas et al., 1995; Simoneit et al., 1999). However, some of these compound series are indicative of species specific biomass burning, when coupled with the directly emitted and thermally altered biomarker compounds. They can collectively be used as specific tracers for assessing and tracking emissions from burning of deciduous tree fuel.

Some deciduous tree smoke samples contain unique biomarkers which may be useful as species specific tracers. For example, Eucalyptus smoke contains lup-2,22(29)-dien-28-al, 24-norolean-2,12-en-28-oic acid, oleana-2,12-dien-28-oic acid and ursana-2,12-dien-28-oic acid. These triterpenoid natural product derivatives are not present in the other deciduous tree smoke samples, thus they are unique tracers in smoke from this species. Oregon Maple smoke has the triterpenoids  $\alpha$ -amyrin,  $\beta$ -amyrin, ursana-2,20-diene, oleana-2,12-diene and lup-1,22(29)-dien-3-one as unique tracers. Red Alder smoke contains 3 $\alpha$ -lupeol, 3 $\beta$ -lupeol, glutin-5-en-3-one, olean-13(18)-en-3-one, taraxerone, isomultifluorenone, 3-methoxylupa-2,22(29)-diene, dihydronycanthanoic acid, olean-13(18)-en-3-one-28-oic acid and 29-chlorolup-1-en-3-one as unique tracers. Silver Birch smoke has sesquiterpenoids which include caryophylla-2(12),5-dien-13-aldehyde, a sesquiterpanol and geigerone, and the triterpenoids allobetul-2-ene and lup-2,22(29)-dien-28-oic acid as unique tracers. The steroid alteration products stigmasta-3,5-diene, stigmasta-4,6-diene and 24-ethylcholesta-4,22-diene are also found in Silver Birch smoke. Dwarf Birch smoke shows the triterpenoids des-A-allobetulin, a nortriterpene, a triterpadiene, a nortriterpenone, 24-norursana-2,12-dien-28-oic acid and the steroid stigmasta-3,5-dien-7-one as tracers. The unique biomarkers are useful as indicative tracers of species specific biomass burning.

The relative abundances (%) of key biomarkers from deciduous tree smoke may be used to distinguish fuel type. Table 5 shows 8 key biomarkers derived mostly from internal plant components (levoglucosan,  $\beta$ -sitosterol, vanillic acid, syringic acid and triterpenoids) and epicuticular wax lipids (heptacosane, docosanoic acid and again triterpenoids). The distributions of these compounds relative to one another are different and represent the unique chemical and physical characteristics among deciduous tree species. It should be noted that triterpenoids are primarily constituents of angiosperms (Kulshreshtha et al., 1972; Pant and Rastogi, 1979; Simoneit, 1986). The absence of the amyrins and their derivatives, coupled with the presence of betulin and derivatives (lupanoids) in the birch smoke samples is a distinguishing feature for birch wood fuels. Also, the

presence of triterpenoids is a distinguishing feature for smoke from angiosperms in contrast to soft woods (i.e. conifers). Thus, the relative abundances of key biomarkers and homologous series compounds reported here can collectively be used as specific tracers for assessing and tracking emissions from burning of deciduous tree fuels.

#### 4. Conclusions

This work reports the lipid and molecular biomarker components in smoke from burning of biomass from 6 deciduous trees (angiosperms). The data is of use for assessing direct organic composition signatures for particle emissions from deciduous tree fuel types during biomass burning. The abundance order for the major compound classes in deciduous tree smoke samples was identified as the following: carboxylic acids > *n*-alkanes > methoxyphenols > *n*-alkenes > triterpenoids > *n*-alkanones > PAH > anhydrosaccharides > steroids > alkylcyclohexanes > *n*-alkanols. Variations in this molecular group order exist among the deciduous tree species burned, however, these are only minor and usually occur between close ranking molecular groups. Although the concentrations of organic compounds in smoke aerosols are highly variable and dependent on combustion temperature, aeration, and moisture content of the source fuel, the biomarkers and their combustion alteration products are source specific. The major biomarkers identified in the smoke samples are useful as tracers for distinguishing the deciduous tree burning component in atmospheric aerosol source attributions.

The range of the MP:P ratio determined for the deciduous tree smoke samples is 0.5–1.5 (average = 1.0), which may be useful for distinguishing deciduous tree burning emissions from fossil fuel and other combustion emissions, and from street and urban dusts. The MP:P range is proposed here as a potential indicator for identifying deciduous tree burning emissions in atmospheric and other environmental samples. Additionally, the average U:R ratio for deciduous tree burning emissions (0.7) may also be of use for distinguishing this source from fossil fuel-derived combustion emissions (e.g. coal combustion, gasoline and diesel engine exhaust). The ratio also suggests that deciduous tree and other biomass burning emissions are significant contributors of particle bound immature organic matter (UCM) present in the atmosphere of rural areas of the western United States. The OC/EC ratios measured for deciduous tree smoke samples range from 9 to 43 (average = 23.6). The distribution indicates that the OC/EC ratios may also be useful to distinguish this source from petroleum derived combustion emissions, such as those found in rural and urban areas, and from natural emissions found in remote areas.

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